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Synthesis and Electrochemical Behavior of Some New Four Coordinated IIB Transition Metal Ions Complexes

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Bis((E)3-(2-nitrophenyl)acrylaldehydene)ethane-1,2-diamine (L) and some its new zinc, cadmium(II) and mercury(II) coordination compounds were prepared in 1:1 ratio of ligand to metal and characterized by elemental analysis, conductometry, electronic spectra, Infra-red spectra, hydrogen and carbon nuclear magnetic resonance spectra. The notable signal changes at Infra-red and nuclear magnetic resonance spectra of the complexes with respect to uncoordinated ligand confirm binding of organic ligand and other anions(X^-) to metal centers. The spectral data and conductivity measurements suggested non-electrolyte nature for all complexes. Furthermore, the redox potentials of ligand and its complexes were studied by cyclic voltammetry (CV) technique in non-aqueous media (DMF). The ligand and its zinc, cadmium and mercury complexes were found to be electro-active in the range of -2.0 to 1.5 volts. Ligand is suggested to be reduced and/or oxidized via three cathodic and three anodic potentials. Zinc iodide, cadmium bromide and iodide showed different redox behavior with respect to free ligand. Other complexes exhibited similar electrochemical redox but with observable changes in compared to uncoordinated ligand.

Keywords: Coordination, Spectroscopic, Cyclic voltammetry, IIB metal ion.

1. INTRODUCTION

Schiff-base ligands and especially their coordination compounds are of attention for chemists due to their structural, spectroscopic, and physicochemical properties that are often related to the nature of the ligand. During the studies on these compounds, several properties were reported for them. Biological activities such as acting as antibacterial, antimicrobial, anti-viral and anticancer [1-4] are a part of important properties of Schiff bases and their coordination compounds. In catalysis point of view, some Schiff base complexes act as catalyst for some transformation such as hydroxylation [5], isomerization [6], decarboxylation [7, 8], and epoxidation [9]. Recently we reported some applications of Schiff bases and their complexes in analytical chemistry [10-13]. Study of electrochemical behavior of a compound can be important in various aspects and also may be lead to some structural information and even chemical and biochemical activity [14-15]. Some researches on the electrochemical properties of some Schiff base compounds have been presented [16-19]. In continuation of our previous works [20-23] on synthesis and characterization of Schiff base complexes, herein we report synthesis, characterization and redox behaviors of bis((E)3-(2-nitrophenyl)acrylaldehydene)ethane-1,2-diamine (L) as a bidentate chelating agent and its new zinc, cadmium(II) and mercury(II) halide complexes.

2. EXPERIMENTAL

2.1. Materials and methods

(E)-3-(2-nitrophenyl)acrylaldehyde, ethylenediamine, zinc, cadmium and mercury halides and other chemicals were provided from Aldrich, Merck or BDH Chemicals. IR spectra were obtained in range of the 4000–400 cm^{-1} as KBr disks. DMF solutions of compounds were used for recording of electronic spectra on a JASCO-V570 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained using a Brucker DPX FT-NMR spectrometer at 500 MHz in DMSO-d$_6$. Melting points were measured by BUCHI B-545 instrument. Molar conductivities of 10^{-3} M solutions of compounds in DMF were recorded using Metrohm-712 conductometer with a dip-type conductivity cell made of platinum black.

2.2. Redox behavior recording

Cyclic voltammograms (CV) were obtained by using a SAMA Research Analyzer M-500. Three electrodes were placed in this instrument, a glassy carbon working electrode, a platinum disk auxiliary electrode and Ag/Ag+ as reference electrode. The glassy carbon working electrode (Metrohm 6.1204.110) with 2.0 ± 0.1 mm diameter was manually cleaned with 1μm alumina polish prior to each scan. The solutions of 10^{-3} M of ligand and complexes in dry DMF as well as tetrabutylammonium hexafluorophosphate as supporting electrolyte were used for record of CV. The solutions were deoxygenated by purging with Ar for 5min. Scan rate was of 0.1 V/S.

2.3. Synthesis of ligand (L)

Bis((E)3-(2-nitrophenyl)acrylaldehydene)ethane-1,2-diamine was prepared similar to our previous report [16] by the reaction between 2 mmol of ethane-1,2-diamine and 4 mmol of (E)-3-(2-nitrophenyl)acrylaldehyde in absolute ethanol (25 mL) under severe stirring for 1.5 hours. The yellowish white precipitate was obtained in 63.42%. Some characteristic infra-red vibrations and electronic transition bands are collected in Table 1. Some physical, suggested assignments for ^{1}H and ^{13}C NMR data of ligand based on figure 1 are seen in below:

^{1}HNMR($CDCl_3$): Yield: 43.42%; Pale Yellowish white precipitate, %$C_{20}H_{18}N_4O_4$: calc. C, 63.48%; H, 4.79%; N, 14.81%; found: C, 63.7%; H, 4.6%; N, 14.9%. ^{1}H NMR: 8.13 (d, $2H_{bb'}$, J = 8.78 Hz), 7.99 (d, $2H_{hh'}$, J = 8.14 Hz), 7.66 (d, $2H_{ee'}$, J = 7.74 Hz), 7.64 (t, $2H_{ff'}$, J = 7.16 Hz and J = 7.22 Hz), 7.47 (d, $2H_{dd'}$, J = 15.99 Hz), 7.48 (t, $2H_{gg'}$, J = 5.80 Hz and J = 10.19 Hz), 6.88 (dd, $2H_{cc'}$, J=15.85 Hz, J=8.81Hz), 3.91 (s, $4H_{aa'}$) ppm. ^{13}CNMR($CDCl_3$): 163.56($C_{2,2'}$), 147.97($C_{10,10'}$), 136.24($C_{4,4'}$), 133.39($C_{9,9'}$), 132.80($C_{5,5'}$), 131.40($C_{3,3'}$), 129.34($C_{6,6'}$), 128.45($C_{7,7'}$), 124.83($C_{8,8'}$), 61.65($C_{1,1'}$) ppm. MS(m/z): 317(M^+). m.p. = 161.71 °C (dec.). Λ_M(DMF): 6.68 $cm^2\ \Omega^{-1}\ M^{-1}$.

2.4. Synthesis of metal complexes

The metal complexes were synthesized and purified similar to our previous report [16, 23]. Some physical and IR data were collected in Table 1 and 2. The suggested assignments for ^{1}H and ^{13}C NMR data of complexes regarding figure 1 are listed in below:

[$ZnLCl_2$]: Yield: 81%; White precipitate. C, 46.67%; H, 3.53%; N, 10.89%; found: C, 46.8%; H, 3.7%; N, 10.9%.^{1}HNMR ((CD_3)$_2$SO): 8.35 (d, $2H_{bb'}$, J = 8.85 Hz), 8.03 (d, $2H_{hh'}$, J = 8.10 Hz), 7.80 (d, $2H_{ee'}$, J = 7.50 Hz), 7.77 (t, $2H_{ff'}$, J = 7.70 Hz), 7.63 (t, $2H_{gg'}$, J = 7.30 Hz), 7.57 (d, $2H_{dd'}$, J = 15.70 Hz),7.01 (dd, $2H_{cc'}$, J=15.68 Hz and J =8.98 Hz), 3.84 (s, $4H_{aa'}$) ppm. ^{13}CNMR ((CD_3)$_2$SO): 166.46($C_{2,2'}$), 147.94($C_{10,10'}$), 139.20($C_{4,4'}$), 133.90($C_{9,9'}$), 130.52($C_{5,5'}$), 129.93($C_{3,3'}$), 128.41($C_{6,6'}$), 128.41($C_{7,7'}$), 124.70($C_{8,8'}$), 59.22($C_{1,1'}$) ppm. m.p. = 270 °C (dec.). Λ_M(DMF): 13.33 $cm^2\ \Omega^{-1}\ M^{-1}$.

[$ZnLBr_2$]: Yield: 79%; Pale Yellow precipitate. ^{1}HNMR ((CD_3)$_2$SO): 8.37 (d, $2H_{bb'}$, J = 8.95 Hz), 8.04 (d, $2H_{hh'}$, J = 8.00 Hz), 7.82 (d, $2H_{ee'}$, J = 6.65 Hz), 7.78 (t, $2H_{ff'}$, J = 7.48 Hz), 7.63 (t, $2H_{gg'}$, J = 7.62 Hz), 7.58 (d, $2H_{dd'}$, J = 15.75 Hz), 7.04 (dd, $2H_{cc'}$, J=15.70 Hz and J = 9.00 Hz), 3.84 (s, $4H_{aa'}$). ^{13}CNMR ((CD_3)$_2$SO): 166.12($C_{2,2'}$), 147.93($C_{10,10'}$), 138.93($C_{4,4'}$), 133.86($C_{9,9'}$), 130.59($C_{5,5'}$), 130.47($C_{3,3'}$), 129.94($C_{6,6'}$), 128.35($C_{7,7'}$), 124.67($C_{8,8'}$), 59.26($C_{1,1'}$) ppm. m.p.= 270.82 °C (dec.). Λ_M(DMF): 13.28 $cm^2\ \Omega^{-1}\ M^{-1}$.

[$ZnLI_2$]: Yield: 75%; Cream precipitate. ^{1}HNMR ((CD_3)$_2$SO): 8.28 (d, $2H_{bb'}$, J = 8.85 Hz), 8.02 (d, $2H_{hh'}$, J = 8.05 Hz), 7.76 (d, $2H_{ee'}$, J = 7.65 Hz), 7.76 (t, $2H_{ff'}$, J = 7.60 Hz), 7.61 (t, $2H_{gg'}$, J = 7.68 Hz), 7.48 (d, $2H_{dd'}$, J = 15.80 Hz), 7.03 (dd, $2H_{cc'}$, J=15.78 Hz and J = 8.87 Hz), 3.80 (s, $4H_{aa'}$). ^{13}CNMR ((CD_3)$_2$SO): 165.27($C_{2,2'}$), 147.95($C_{10,10'}$), 137.94($C_{4,4'}$), 133.78($C_{9,9'}$), 131.06($C_{5,5'}$), 130.34($C_{3,3'}$), 129.99($C_{6,6'}$), 128.36($C_{7,7'}$), 124.62($C_{8,8'}$), 59.71($C_{1,1'}$) ppm. m.p.= 282.12 °C (dec.). Λ_M(DMF): 12.31 $cm^2\ \Omega^{-1}\ M^{-1}$.

[$CdLCl_2$]: Yield: 83%; White precipitate. ^{1}HNMR ((CD_3)$_2$SO): 8.26 (d, $2H_{bb'}$, J = 8.65 Hz), 8.02 (d, $2H_{hh'}$, J = 8.10 Hz), 7.90 (d, $2H_{ee'}$, J = 7.75 Hz), 7.77 (t, $2H_{ff'}$, J = 7.55 Hz and J = 7.65 Hz), 7.62 (t, $2H_{gg'}$, J = 7.90 Hz and J = 7.70 Hz), 7.45 (d, $2H_{dd'}$, J = 15.80 Hz), 7.35 (dd, $2H_{cc'}$, J=15.32 Hz and J = 8.78 Hz), 3.78 (s, $4H_{aa'}$). ^{13}CNMR ((CD_3)$_2$SO): 165.19($C_{2,2'}$), 148.00($C_{10,10'}$), 137.10($C_{4,4'}$), 133.64($C_{9,9'}$), 131.87($C_{5,5'}$), 130.19($C_{3,3'}$), 130.09($C_{6,6'}$), 128.40($C_{7,7'}$), 124.58($C_{8,8'}$), 60.38($C_{1,1'}$) ppm. m.p. = 245.16 °C (dec.). Λ_M(DMF): 11.22 cm^2 Ω^{-1} M^{-1}.

[$CdLBr_2$]: Yield: 76%; Yellow precipitate. calc. C, 36.92%; H, 2.79%; N, 8.61%; found: C, 37.1%; H, 2.9%; N, 8.7%.^{1}HNMR (($(CD_3)_2SO$): 8.26 (d, 2$H_{bb'}$, *J* = 8.80 Hz), 8.03 (d, 2$H_{hh'}$, *J* = 8.00 Hz), 7.89 (d, 2$H_{ee'}$, *J* = 7.50 Hz), 7.77 (t, 2$H_{ff'}$, *J* = 7.55 Hz and *J* = 7.60 Hz), 7.63 (t, 2$H_{gg'}$, *J* = 7.72 Hz and *J* = 7.45 Hz), 7.44 (d, 2$H_{dd'}$, *J* = 15.80 Hz), 7.26 (dd, 2$H_{cc'}$, *J*=15.86 Hz and *J* = 8.80 Hz), 3.78 (s, 4$H_{aa'}$). ^{13}CNMR ($(CD_3)_2SO$): 164.87($C_{2,2'}$), 147.99($C_{10,10'}$), 136.88($C_{4,4'}$), 133.63($C_{9,9'}$), 131.88($C_{5,5'}$), 130.15($C_{3,3'}$), 130.11($C_{6,6'}$), 128.41($C_{7,7'}$), 124.57($C_{8,8'}$), 60.51($C_{1,1'}$) ppm. m.p. = 226.73 °C (dec.). Λ_M(DMF): 11.01 cm^2 Ω^{-1} M^{-1}.

[$CdLI_2$]: Yield: 80%; Cream precipitate. ^{1}HNMR ($(CD_3)_2SO$): 8.27 (d, 2$H_{bb'}$, *J* = 8.85 Hz), 8.02 (d, 2$H_{hh'}$, *J* = 8.10 Hz), 7.89 (d, 2$H_{ee'}$, *J* = 7.45 Hz), 7.77 (t, 2$H_{ff'}$, *J* = 7.55 Hz and *J* = 7.65 Hz), 7.61 (t, 2$H_{gg'}$, *J* = 7.75 Hz), 7.46 (d, 2$H_{dd'}$, *J* = 15.80 Hz), 7.22 (dd, 2$H_{cc'}$, *J*=15.00 Hz and *J* = 9.15 Hz), 3.79 (s, 4$H_{aa'}$). ^{13}CNMR ($(CD_3)_2SO$): 164.94($C_{2,2'}$), 147.97($C_{10,10'}$), 137.06($C_{4,4'}$), 133.65($C_{9,9'}$), 131.76($C_{5,5'}$), 130.18($C_{3,3'}$), 130.11($C_{6,6'}$), 128.40($C_{7,7'}$), 124.60($C_{8,8'}$), 60.41($C_{1,1'}$) ppm. m.p. = 257.18 °C (dec.). Λ_M(DMF): 8.89 cm^2 Ω^{-1} M^{-1}.

[$HgLCl_2$]: Yield: 88%; White precipitate. ^{1}HNMR ($(CD_3)_2SO$): 8.45 (d, 2$H_{bb'}$, *J* = 10.10 Hz), 8.04 (d, 2$H_{hh'}$, *J* = 8.00 Hz), 7.87 (d, 2$H_{ee'}$, *J* = 7.80 Hz), 7.79 (t, 2$H_{ff'}$, *J* = 6.65 Hz and *J* = 7.35 Hz), 7.64 (t, 2$H_{gg'}$, *J* = 7.10 Hz and *J* = 7.95 Hz), 7.57 (d, 2$H_{dd'}$, *J* = 16.30 Hz), 7.14 (dd, 2$H_{cc'}$, *J*=15.00 Hz and *J*=7.50 Hz), 3.86 (s, 4$H_{aa'}$). ^{13}CNMR ($(CD_3)_2SO$): 166.20($C_{2,2'}$), 148.00($C_{10,10'}$), 138.82($C_{4,4'}$), 133.79($C_{9,9'}$), 130.94($C_{5,5'}$), 130.48($C_{3,3'}$), 129.93($C_{6,6'}$), 128.48($C_{7,7'}$), 124.66($C_{8,8'}$), 59.93($C_{1,1'}$) ppm. m.p. = 187.51 °C (dec.). Λ_M(DMF): 7.64 cm^2 Ω^{-1} M^{-1}.

[$HgLBr_2$]: Yield: 81%; Light Yellow precipitate. ^{1}HNMR ($(CD_3)_2SO$): 8.54 (d, 2$H_{bb'}$, *J* = 8.85 Hz), 8.06 (d, 2$H_{hh'}$, *J* = 8.00 Hz), 7.85 (d, 2$H_{ee'}$, *J* = 6.65 Hz), 7.82 (t, 2$H_{ff'}$, *J* = 7.25 Hz and *J* = 7.55 Hz), 7.66 (t, 2$H_{gg'}$, *J* = 7.72 Hz and *J* = 7.40 Hz), 7.64 (d, 2$H_{dd'}$, *J* = 15.70 Hz), 7.12 (dd, 2$H_{cc'}$, *J*=15.65 Hz and *J* = 8.86 Hz), 3.88 (s, 4$H_{aa'}$). ^{13}CNMR ($(CD_3)_2SO$): 166.79($C_{2,2'}$), 148.00($C_{10,10'}$), 139.85($C_{4,4'}$), 133.91($C_{9,9'}$), 130.68($C_{5,5'}$), 130.30($C_{3,3'}$), 129.86($C_{6,6'}$), 128.43($C_{7,7'}$), 124.75($C_{8,8'}$), 59.61($C_{1,1'}$) ppm. m.p. = 180.17 °C (dec.). Λ_M(DMF): 9.96 cm^2 Ω^{-1} M^{-1}.

[$HgLI_2$]: Yield: 89%; Pale Yellow precipitate. %$C_{20}H_{18}HgI_2N_4O_4$: calc. C, 28.84%; H, 2.18%; N, 6.73%; found: C, 29.1%; H, 2.3%; N, 6.9%. ^{1}HNMR ($(CD_3)_2SO$): 8.55 (d, 2$H_{bb'}$, *J* = 8.85 Hz), 8.07 (d, 2$H_{hh'}$, *J* = 8.10 Hz), 7.82 (d, 2$H_{ee'}$, *J* = 3.85 Hz), 7.66 (t, 4H(2$H_{ff'}$, 2$H_{gg'}$), *J* = 5.00 Hz and *J* = 4.10 Hz), 7.66 (d, 2$H_{dd'}$, *J* = 15.80 Hz), 7.08 (dd, 2$H_{cc'}$, *J*=15.62 Hz and *J* = 8.92 Hz), 3.86 (s, 4$H_{aa'}$). ^{13}CNMR ($(CD_3)_2SO$): 166.53($C_{2,2'}$), 147.97($C_{10,10'}$), 139.92($C_{4,4'}$), 133.97($C_{9,9'}$), 130.72($C_{5,5'}$), 129.94($C_{3,3'}$), 129.88($C_{6,6'}$), 128.32($C_{7,7'}$), 124.80($C_{8,8'}$), 59.56($C_{1,1'}$) ppm. m.p. = 185.26 °C (dec.). Λ_M(DMF): 11.01 cm^2 Ω^{-1} M^{-1}.

3. RESULTS AND DISCUSSION

3.1. Physical and analytical data

Elemental analysis of selected compounds and some its physical parameters have been presented in experimental section. Analytical data confirm the 1:1 ratio of ligand to metal salt. The ligand and its complexes are soluble in organic solvents such as dimethylformamide and dimethylsulfoxide and insoluble alcohols such as methanol and ethanol. Melting point of ligand is at 161.71 °C. The complexes are decomposed in the range of 180.17-282.12 °C. The proposed structure for the complexes is depicted in figure 1. Conductivity measurement of complexes in DMF solution results that the molar conductivities of them are in the range of 6.68-13.33 $cm^2\ \Omega^{-1}M^{-1}$ indicating non-electrolyte nature of them. These low values of conductivities well prove coordination of all ligands especially halide anions to metal center and the complexes are considerably stable and don’t dissociate in solution. On the other hand, the proposed structure is in agreement with our recently reported x-ray single crystal of zinc chloride complex (figure 2)[24].

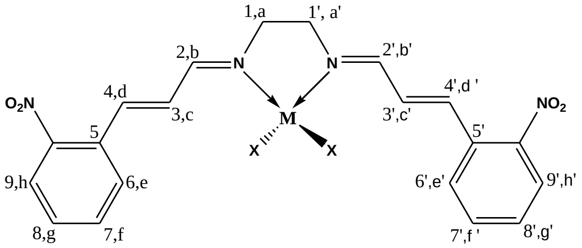


Figure 1. Proposed structure of ligand and its complexes (M=Zn, Cd, Hg; X=Cl, Br and I).

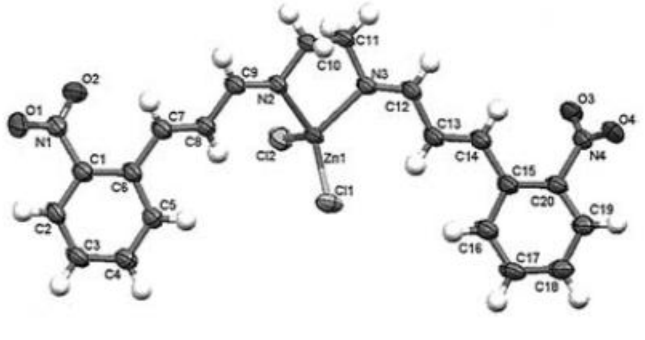


Figure 2. ORTEP structure of zinc chloride complex.

3.2. Vibrational spectroscopy

Some important vibrational frequencies of the bidentate ligand and its zinc, cadmium and mercury complexes have been collected in the Table 1. The ligand absorption frequency at 2864 cm^{-1} is related to C-H of iminic group. This vibration is appeared at 2877-2888 cm^{-1} in the complexes.

Imine group (C=N) of ligand is seen at 1624 cm^{-1} [20-26]. After binding of ligand to metal center, this characteristic vibration is shifted to higher wave numbers by 6-15 cm^{-1} as well as enhancing of its intensity. Two other important vibration frequencies are related to asymmetric and symmetric stretching of nitro groups. They are appeared at 1519 and 1347 cm^{-1} in the ligand spectrum respectively [27]. After coordination, these asymmetric and symmetric vibrational frequencies are appeared at 1519-1528 and 1335-1346 cm^{-1} respectively. Finally it is suggested that asymmetric and symmetric vibrations of metal-nitrogen bond as other evidence for binding of ligand to metal center are seen at 460-490 cm^{-1} as moderate and weak peaks [28].

Table 1. Some characteristic IR peaks (cm^{-1}) and UV-Visible spectral data of ligand (L) and its complexes.

Compound	νCH_{imine}	$\nu C=N$	$\nu M–N$	νNO_2 (asym. and Sym.)	λ_{max} (ε, $M^{-1}cm^{-1}$) (nm)^a
L	2864(m)	1624(s)	-	1519(s), 1347(s)	270(46014),326(11286)
$ZnLCl_2$	2886(w)	1634(vs)	461(m), 438(m)	1528(vs), 1346(s)	270(53115),322(12962)
$ZnLBr_2$	2882(w)	1633(vs)	490(w), 444(w)	1526(vs), 1343(s)	270(52203),321(12474)
$ZnLI_2$	2878(w)	1639(vs)	485(w), 441(w)	1521(vs), 1345(vs)	270(56178),320(13894)
$CdLCl_2$	2879(w)	1636(vs)	491(m),437(w)	1524(vs),1341(vs)	270(46215),324(11640)
$CdLBr_2$	2888(w)	1634(vs)	488(m),445(w)	1522(vs),1342(vs)	270(45885),325(11387)
$CdLI_2$	2880(w)	1635(vs)	486(m),441(m)	1520(vs),1345(vs)	270(48945),324(11973)
$HgLCl_2$	2884(w)	1631(vs)	474(m),445(w)	1519(vs),1344(vs)	270(45474),325(11170)
$HgLBr_2$	2877(w)	1630(vs)	473(w),433(w)	1519(vs),1342(vs)	270(54273),325(11423)
$HgLI_2$	2879(w)	1635(vs)	470(w),439(w)	1520(vs),1335(vs)	270(59263),331(14197)

[a] In DMF

3.3. Electronic spectra

The electronic absorption spectra of the bidentate Schiff base ligand, Zn(II), Cd(II) and Hg(II) halide complexes were recorded at room temperature. The absorption region, spectra wavelengths and their calculated absorption coefficients are given in table 1. The ligand spectrum shows two internal electronic transitions at 270 and 326 nm. These two electronic transitions may be assigned to π-π* transition of aromatic rings or olefinic sections and imine groups respectively. These internal electronic transitions are not affected considerably (1-6 nm) after binding of ligand to metal centers but their absorption coefficients are enhanced smoothly in most of them.

3.4. Nuclear magnetic resonance spectra

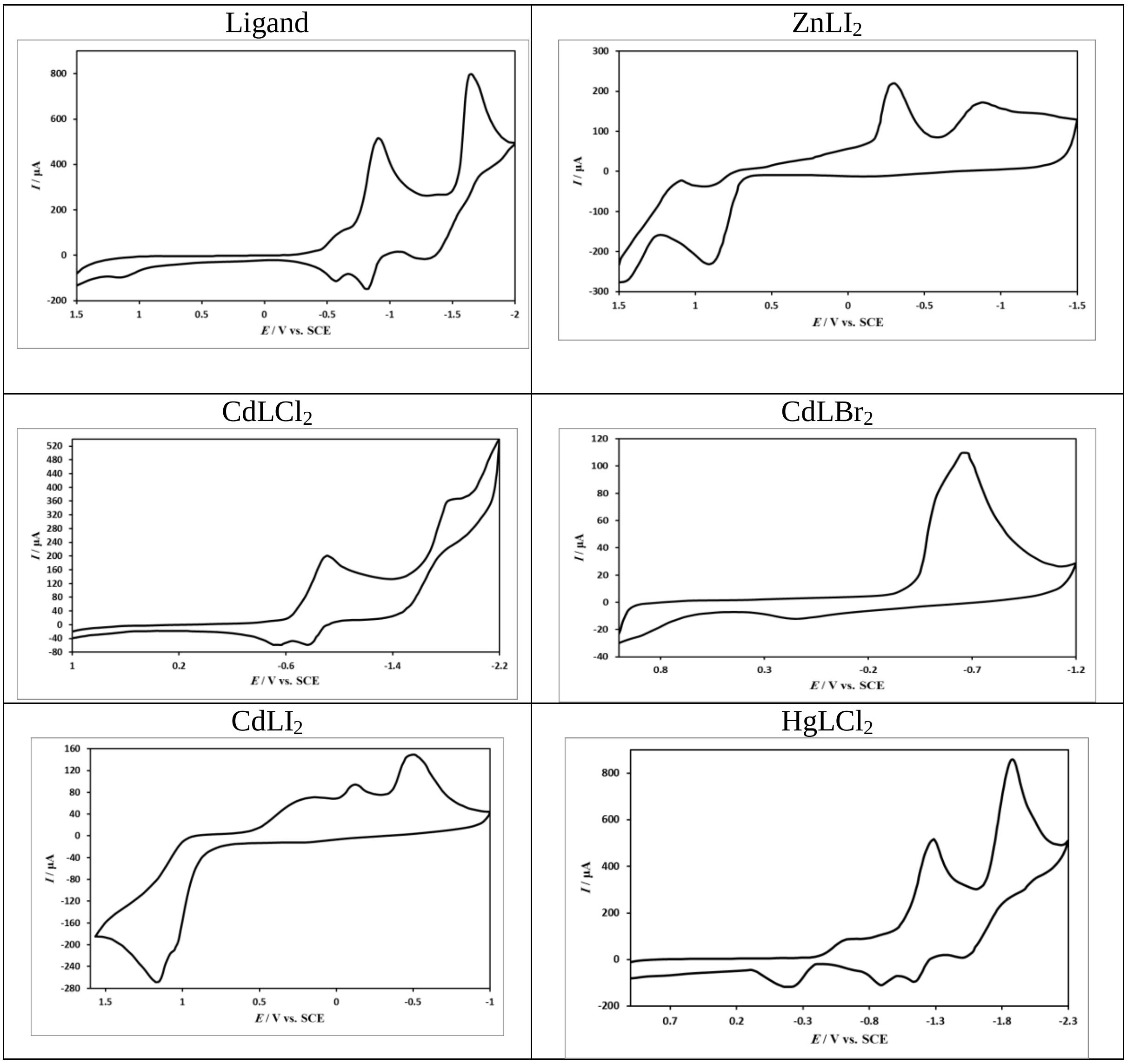
The NMR spectra of the ligand in $CDCl_3$ and Zn, Cd and Hg complexes in $(CD_3)_2SO$ were well in agreement with suggested structure in figure 1. The ^1H NMR spectrum of the ligand, recorded in $CDCl_3$ at 500MHz showed imine protons ($2H_{bb'}$) at 8.13 ppm as a doublet due to coupling with hydrogens of c, c' with coupling constant of 8.78 Hz [20-22, 29]. This iminic proton is appeared as doublet in the range of 8.26-8.37 ppm in zinc and cadmium complexes and in the range of 8.45-8.54

ppm for mercury complexes with coupling constant of 8.65-10.10 Hz. The notable downfielded chemical shifts of imine hydrogens in complexes spectra with respect to free ligand well prove its coordination to metal centers. The higher deshielding of imine hydrogen in mercury complexes indicates stronger binding of ligand in mercury complexes with respect to zinc and cadmium analogues. ^{1}HNMR signals of Hydrogens of h, h' and e, e' of ligand in *ortho* and *meta* positions with respect to nitro-group are seen at 7.99 and 7.66 ppm with coupling constants of 8.14 and 7.74 Hz respectively. These protons are downfielded to 8.02-8.07 ppm after coordination. Nuclear resonance peaks of f,f ' and gg' in ligand spectrum are observed as asymmetric triplet at 7.64 and 7.48 ppm. Again these signals especially gg' shift to weaker magnetic fields at 7.76-7.82 and 7.61-7.66 ppm. It is to be noted that in mercury iodide complex, the hydrogens of f, f ' and g,g' have been found to be the same and are appeared as a triplet at 7.66 ppm. The d, d' olefinic hydrogens of ligand are shown as a doublet at 7.47 ppm between the aromatic hydrogens of f,f' and g,g'. After complexation of ligand, the related signals shift to position before the g,g' hydrogens in all complexes. This is one of obvious change of ligand HNMR after binding. Hydrogens of c,c' are found as doublt of doublet in olefinic region of NMR spectrum of ligand at 6.88 ppm due to coupling with d,d' and b,b' respectively. This splitting pattern is retained at downfielded position viz. 7.01-7.35 ppm except for mercury chloride complex. Furthermore, the ^{13}C NMR spectra of the ligand and complexes were recorded for confirmation of proposed structure. The iminic carbons are appeared at 163.56($C_{2,2'}$) ppm [16, 20-23]. In the complexes, this characteristic signal is placed in the range of 164.87- 166.79 ppm confirming binding of the ligand azomethine groups to metal center. Downfielded or upfielded chemical shifts of other carbon signals as seen at experimental section can be accepted as other evidences for well coordination of Schiff base ligand to metal ions.

3.5. Redox behavior

Cyclic voltammograms (CV) of ligand and its coordination compounds were recorded on glassy carbon electrode with scan rate of 0.1 V/S in dry DMF. The voltammograms of the ligand and its coordination compounds have been presented in figure 3. As shown in figure 3, the ligand and its complexes are redox active at solvent window e.g. -2 to 1.5 volt.

The bidentate Schiff ligand is reducible at negative potentials of -0.65, -0.93 and -1.66 V. In positive wave the ligand is oxidized at -1.33, -0.83 and -0.59 V. The cathodic peaks may be assigned to the reduction of the nitro group to the radical anion and the reduction of the nitro radical anion to the nitroso dianion derivative [30-33]. This electrochemical behavior may be considered as quasi-reversible processes. Zinc iodide, cadmium bromide and cadmium iodide complexes show different behaviors in their voltammograms with respect to free ligand. Zinc iodide complex is reduced at -0.32 and -0.87 V and only oxidized at 0.89 V. Cadmium bromide complex is only reduced at -0.68 V. Cathode peaks of cadmium iodide complex are appeared at 0.19, -0.14 and -0.51 V while the complex is oxidized at anodic potentials of 1.04(shoulder) and 1.14 V. It seems that coordination of ligand in these complexes leads to elimination and/or ease of reduction in negative direction and resistance to oxidation in reverse sweeping. Cadmium chloride, mercury chloride, bromide and iodide complexes exhibit redox behavior nearly similar free ligand. Cadmium chloride is reducible at two cathodic peaks; -0.93 and -1.84 V and oxidizable at two anodic waves; -0.78 and -0.57 V. One cathodic and one anodic potential has been omitted in this complex with respect to free ligand meanwhile the second cathodic peak has been appeared at more negative value and anodic peaks smoothly has been shifted toward positive numbers. The reduction of mercury chloride is occurred at three potentials; -0.63, -1.3 and -1.89 V similar to free ligand but at more negative values for second and third peaks. But in anodic sweeping, this compound is oxidized in four steps at -1.55, -1.15, -0.88 and -0.21 V showing one step more than uncoordinated ligand. In voltammograms of mercury bromide and iodide complexes, two reduction waves are observed at -1.31 and -2.04 V for before and -1.29 and -2.00 V for after respectively. In positive potential direction, mercury bromide is oxidized at -1.18 and -0.92 V meanwhile the mercury iodide show its oxidation signals at -1.14 and -0.90 V. The observed cathodic and anodic potentials in these two complexes reveal that coordinated ligand is reduced harder and oxidized easier with respect to free situation. This result confirms well coordination of ligand to mercury ion and then strongly *pi*-back bonding from metal to ligand orbitals that lead to an increase of electron density on coordinated ligand structure and therefore may be responsible for obtained results.



Ligand

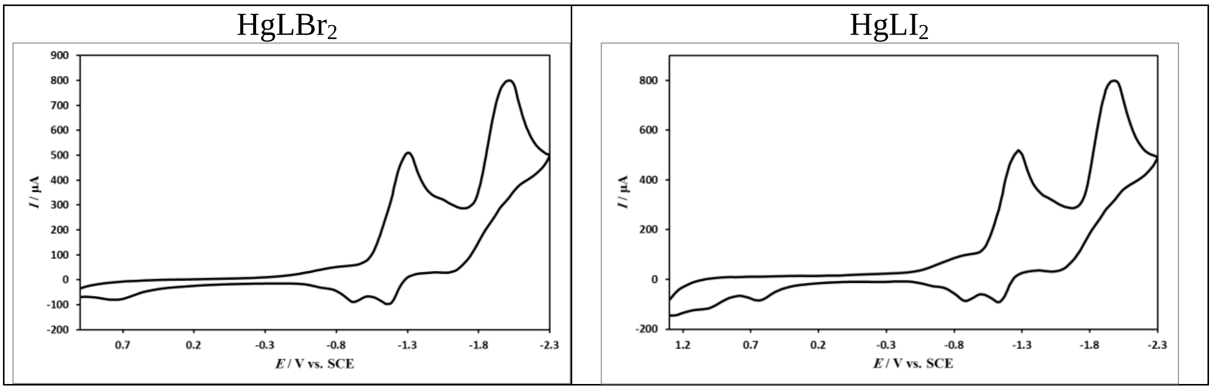
$ZnLI_2$

$CdLCl_2$

$CdLBr_2$

$CdLI_2$

$HgLCl_2$


$HgLBr_2$

$HgLI_2$

Figure 3. CV diagrams of ligand and its complexes.

4. CONCLUSION

In this work, we reported the synthesis, spectral characterization and electrochemical behavior of a bidentate chelating ligand and its zinc(II), cadmium(II) and mercury(II) halide complexes. The physical and spectral data well confirm binding of the ligand and halide anions in pseudo- tetrahedral geometry. The electrochemical behavior of the complexes in compared to ligand was described. The ligand has been found to be reduced and /or oxidized at three cathodic and anodic potentials. Zinc iodide, cadmium bromide and iodide complexes exhibited different voltammograms with respect to free ligand while other complexes showed redox behavior nearly similar to free ligand but with some observable changes in cathodic and anodic potentials.

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References

1. R. Nair, A. Shah, S. Baluja and S. Chanda, *J. Serb. Chem. Soc.,* 71 (7) (2006) 733.
2. K. Santosh, M. S. Niranjan, K. C. Chaluvaraju, C. M. Jamakhandi and K. Dayanand, *J. Curr. Pharm. Res.*, 1 (2010) 39.
3. M. Jesmin, M. M. Ali and J. A. Khanam, *Thai J. Pharm. Sci.,* 34 (2010) 20-31.
4. A. Jarrahpour, D. Khalili, E. DeClercq, C. Salmi and J. Michel Brunel, *Molecules,* 12 (2007*)* 1720.
5. J. S. Baik, S.-B. Han and N. H. Lee, *Bull. Korean Chem. Soc.*, 27 (2006) 333.
6. F. Ding, S. V. Doorslaer, P. Cool and F. Verpoort, *Appl. Organomet. Chem.,* 25(8) (2011) 601.
7. M. Montazerozohori, M. Nasr-Esfahani and P. Akhlaghi, *Chin. J. Chem.,* 27 (2009) 1007.
8. M. Montazerozohori, M. H. Habibi, L. Zamani-Fradonbe and S. A. R. Musavi, *Arkivoc,* (xi) (2008) 238.
9. K. Ambroziak, R. Pelech, E. Milchert, T. Dziembowska and Z. Rozwadowski, *J. Mol. Catal. A: Chem.,* 211 (2004) 9.
10. M. Ghaedi, F. Ahmadi, Z. Tavakoli, M. Montazerozohori, A. Khanmohammadi and M. Soylak, *J. Hazard. Mater.*, 152 (2008) 1248.
11. M. Ghaedi, M. Montazerozohori, A. Mousavi, S. Khodadoust and M. Mansouri, *Mater. Sci. Engin. C,* 32 (2012) 523.

12. M. Ghaedi, H. Khajehsharifi, M. Montazerozohori, H. Tavallalib, K. Tahmasebi and S. Khodadust, *Mater. Sci. Engin. C*, 32 (2012) 674.
13. M. Ghaedi, M. Montazerozohori, Z. Andikaey, A. Shokrollahi, S. Khodadoust, M. Behfar and S. Sharifi, *Int. J. Electrochem. Sci.*, 6 (2011) 4127.
14. J. M. Kauffmann and J. C.Vire, *Anal. Chim. Acta*, 273 (1993) 329.
15. J. Wang, (Ed.) *Electroanalytical Techniques in Clinical Chemistry and Laboratory Medicine*, VCH, New York, (1988).
16. M. Montazerozohori, M. Sedighipoor and S. Joohari, *Int. J. Electrochem. Sci.*, 7 (2012) 77.
17. A. D. Kulkarni, S. A. Patil and P. S. Badami, *Int. J. Electrochem. Sci.*, 4 (2009) 717.
18. P. A. M. Farias and M. B. R. Bastos, *Int. J. Electrochem. Sci.*, 4 (2009) 458.
19. S. Ershad, L.-A. Sagathforoush, G. Karim-nezhad and S. Kangari, *Int. J. Electrochem. Sci.*, 4 (2009) 846.
20. M. Montazerozohori and M. Sedighipoor, *Spectrochim. Acta Part A*, 96 (2012) 70.
21. M. Montazerozohori and S.A. Musavi, *J. Coord. Chem.*, 61 (2008) 3934.
22. M. Montazerozohori, S. Khani, H. Tavakol, A. Hojjati and M. Kazemi, *Spectrochim. Acta Part A*, 81(1) (2011) 122.
23. M. Montazerozohori, S. Joohari and S.A. Musavi, *Spectrochim. Acta Part A*, 73 (2) (2009) 231.
24. M. H. Habibi, M. Montazerozohori, A. Lalegani, R. W. Harrington and W. Clegg, *Anal. Sci.*, 23 (2007) X51.
25. G. G. Mohamed, M. M. Omar and A. M. Hindy, *Turk. J. Chem.*, 30 (2006) 361.
26. V. S. V. Satyanarayana, P. Sreevani, A. Sivakumar and V. Vijayakumar, *Arkivoc*, xvii (2008) 221.
27. N. Sundaraganesan, , S. Ilakiamani, H. Saleem, P. M. Wojciechowski and D. Michalski, *Spectrochim. Part Acta A*, 61 (2005) 2995.
28. K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, New York:Wiley, 3rd edn(1997).
29. S. Dehghanpour, A. H. Mahmoudkhani and A. M. Amirnasr, *Struct. Chem.*, 17 (2006) 255.
30. J. A. Squella, P. Gonzalez, S. Bollo and L. J. Núnez-Vergara, *Pharm. Res.*, 16 (1999) 161.
31. C. Yanez, J. Pezoa, M. Rodriguez, L. J. Nùnez-Vergara and J. A. Squella, *J. Electrochem. Soc.*, 152 (2005) 146.
32. S. Bollo, L. J.Núnez-Vergara, C.Martinez, G.Chauviere, J. Périé and J. A. Squella, *Electroanal.*, 15 (2003) 19.
33. S. Bollo, L. J. Núnez-Vergara, C. Barrientos and J. A. Squella, *Electroanal.*, 17 (2005) 1665.